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**SANDIA NATIONAL LABORATORIES
CIVILIAN RADIOACTIVE WASTE MANAGEMENT
TECHNICAL PROCEDURE (TP)**

TP-265

Borehole Water Sampling in the Exploratory Studies Facility

Revision 02

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(Reviewer signatures above serve to document the review and resolution of comments)

REVISION HISTORY

<u>Rev.</u>	<u>Summary of Changes</u>
00	Initial Issue
01	Revised to address administrative errors identified from a project-related self-assessment.
02	Revised to add ‘approval’ signature. No change to revision 01 text.

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1.0 SCOPE

This procedure describes water-sampling methods from specially constructed boreholes associated with underground thermal tests at Yucca Mountain (YM). Samples will be collected for analysis of major ion chemistry and determination of isotopic compositions. Some field measurements are described for determining unstable chemical parameters. To this end, collection of representative samples, containment in proper vessels, and appropriate preservation measures are discussed. For each sample specified for a particular analysis, the sample requirements and handling are stated explicitly. This document shall be used to control the collection of water samples, the preservation of these samples, and the field testing of borehole waters collected during thermal tests at Yucca Mountain.

The following methods are specified herein:

- 1) the collection and preservation of qualified water samples designated for laboratory analytical data;
- 2) the measurement of selected unstable properties and field analyses of certain chemical constituents;
- 3) and the document control of samples collected and data obtained in the field

This Technical Procedure (TP) applies to all Yucca Mountain Project (YMP) personnel who will be trained and qualified to take these samples.

2.0 OBJECTIVE

This Technical Procedure defines the procedure obtaining water samples from boreholes in the Exploratory Studies Facility (ESF). Generally, drilled boreholes in the Yucca Mountain unsaturated zone are relatively dry and not conducive to standard water-sampling methods. However, thermal field tests being conducted in the ESF elevate the rock temperatures such that water mobilization and redistribution increase moisture saturation in some areas. Boreholes that intersect the higher saturation regions may potentially yield sufficient water to collect for analysis, although limited volumes still restrict the applicable methods for sampling. The protocol herein describes methods of aqueous sampling from boreholes instrumented with inflated packers that separate the holes into several open intervals. Teflon tubing extends from the collar of the borehole to the deepest end of each interval, and peristaltic pumping draws moisture through the tubing into collection vessels. Aqueous sampling in this manner may yield no water, very minor quantities, or several liters of water may be available for collection. The protocol which follows reflects the importance of collecting even small volumes of fluid and prioritizing the samples for both laboratory and field analysis when insufficient quantity is collected for a full suite of testing. In these cases, the lack of ample volumes of fluid from each sampling location, eliminates duplicate testing opportunities, restricts consistency checks in some cases, and because sample is limited, assumes that no sample is lost to flushing the pump lines and filters.

3.0 RESPONSIBILITIES

The Principal Investigator (PI) has responsibility for ensuring that all information obtained in the ESF is in accordance with Sandia National Laboratories (SNL's) Quality Assurance Implementing Procedures (QAIPs) and Technical Procedures (TPs), and that all individuals collecting data are properly trained.

Principal Investigators (PIs) of all activities who choose to work to this procedure shall ensure compliance. Each PI shall require that personnel working to this procedure have appropriate qualifications and experience to satisfactorily perform the work described. PIs are responsible for preparation and revisions of

this TP, and for the maintenance and submittal of records that derive from its implementation. Documentation of work shall include traceable sample chain-of-custody forms entered into the scientific notebook associated with this work and shall fulfill the Quality Assurance (QA) requirements.

4.0 EQUIPMENT

Minimum equipment required:

- 1) Disposable syringes and 0.45 micron (μm) syringe filters. Sampling bags may be required when filter collection is requested.
- 2) At least one peristaltic pump and appropriate power supply. Two or more such pumps may be used (at separate boreholes) to facilitate quicker sampling.
- 3) Tubing, fittings, tee connections and clamps. All components making contact with sample water should be detergent-washed, acid- and DI-rinsed, or purchased equivalently pre-cleaned. Collection flask or vessel. Enough collection vessels for each sampling site or maintain cleaning capabilities in the field for re-use.
- 4) Miscellaneous supplies: scissors or knife for cutting tubing, clock or watch, field notebook, indelible blue or black ink pen, vacuum gauge, extra pump, extension cords, waste collection containers, and trash bags.

Additional equipment needed for certain sampling procedures is listed in section 5.

Bottles purchased as “pre-cleaned” as per laboratory standards (“acid-washed”) or determined to be equivalently clean bottles shall be used. All sampling vessels are to be transported and maintained in a clean state.

5.0 METHOD

Summary of Method:

Sampling from the Drift Scale Test (DST) boreholes: The water will be sampled from the Hydrology boreholes by peristaltic pumping. Most of the boreholes will be horizontal or at slight angles of inclination or declination (usually $< 20^\circ$) from the horizontal. These boreholes are instrumented with inflatable packers that isolate open zones several meters long. Tubing for water and gas sampling extends from the borehole collar to the lowest end of each interval. Condensation, pore waters, and fracture-flow entering the borehole may drain by gravity to the lowest point and accumulate in these intervals and eventually be retrieved by pumping these tubes. From the borehole collar, the tubing extends to a junction box where it attaches to a manifold. The tubes used to pump fluid are 3/8” (O.D.) x 1/4” (I.D.) PTFE Teflon. On the output of the junction box, a 3/8” to 1/2” Swagelock adapter compression fitting is present for attaching larger diameter tubing to the pump situated outside of the boreholes.

5.1 Preparation for sampling: Performance Tests

Use only NIST-traceable standards for calibration and performance tests.

- 1) Calibrate the Ultrameter’s pH meter as per the instrument’s manual. Use pH 4 and pH 7 buffers for calibration, and then record the measurements of pH buffers of values of 4, 7 and 10. If the

recorded value of any standard deviates by more than 0.2 pH units, repeat calibration and re-check.

- 2) Check the calibration of the Ultrameter's Total Dissolved Solids (TDS) meter as per the instrument's manual. Use three standards, one of which shall have a nominal value of <10 PPM, and one of which shall have a nominal value of >300PPM. Record the measured values of the standards. If the measured value deviates from that of the nominal value by more than 10%, recalibrate as per the instrument's manual and re-check.
- 3) Check the calibration of the Ultrameter's conductivity meter as per the instrument's manual. Use three standards, one of which shall have a nominal value of <15 microsiemens, and one of which shall have a nominal value of >450 microsiemens. Record the measured values of the standards. If the measured value deviates from that of the nominal value by more than 10%, recalibrate as per the instrument's manual and re-check.
- 4) Record the results of the calibration checks, as well as the manufacturer, nominal value, lot number, and expiration date of each standard used. Also note the unique M+TE identifying number of the meter, the tolerances of an acceptable check, and whether or not the meter met this criteria.
- 5) Assemble the peristaltic pump(s). Test the pump and clean its tubing by pumping deionized water. Using the Ultrameter, check the TDS level of the pumped water. If the pumped water is greater than 5 PPM, pump more deionized water through the tubing and re-check.

5.2 Sampling

- 1) Between the output side of the junction box and the inlet side of the pump, attach the Tygon tubing. Insert a vacuum gauge into the line using a tee-junction before the peristaltic pump inlet. The tubing length and diameter should be kept to a practical minimum.
- 2) Attach a section of Tygon tubing using a clean barb at the tee-connector to run through the pump and into the sample collection bottle. Length should be kept to a practical minimum (~ 2-4 ft from the pump outlet to bottle). (See section 5.7, collection of carbon isotopes sample, for deviations in sampling protocol.)
- 3) Verify that the pumping assembly is free of leaks and functioning properly: turn the pump on and close the valve at the junction box to isolate the sampling apparatus from the interval. The vacuum gauge reading should rise.
- 4) Open the valve at the junction box and pump for a minimum of 5 minutes. If no sample is obtained, record the date and the starting and ending pumping times, decouple the tubing and sample the next interval, repeating steps 1 through 3. If sample is obtained, obtain field measurements using the Ultrameter. Record the temperature, pH, Total Dissolved Solids (TDS), and conductivity. If the sample has both a TDS of less than 20 PPM and a pH of between 4.5 and 8, it may be presumed to be condensed steam and only one, untreated sample of 60mL need be obtained and stored in a polyethylene bottle. If the field measurements deviate from these parameters, or if the sample is in any way unusual in appearance, continue sampling as needed to meet the maximum volume requirements detailed in Table 1, or until no more sample can be obtained. If sample volume is not sufficient to meet the maximum volume requirements in Table 1 and direct guidance from the PI is not available, collect the default volumes listed in Table 1, with the sample types at the top of the table having the highest priority. Make an additional set of

field measurements for the final sample. All field analyses should be performed as soon as possible.

- 5) Filter the samples using a 0.45 μm syringe-filter. Use a new filter for each interval.
- 6) All filtered samples shall be collected into pre-cleaned collection bottles and promptly labeled. All designated samples should be distributed into appropriate bottles (Table 1). Each bottle will be assigned a sample management facility (SMF) bar code, and notes shall be made to indicate at a minimum the borehole and interval and the collection date/time. If sufficient sample exists, or at the discretion of the PI, a field analysis for Total Alkalinity shall be performed (see section 5.11)
- 7) After sampling a wet interval, pump deionized water through the Tygon tubing until Total Dissolved Solids in the water exiting the pumping assembly reads less than 5 PPM before sampling the next interval. Make sure to pump all rinse water out of the tubing to avoid dilution of the next sample.
- 8) Records of the sampling activities at each site shall be prepared and maintained. For dry intervals or for low volume yields where insufficient quantity exists to sample, the approximate yield shall nevertheless be estimated. Record the date and the starting and ending pump times for each interval. The temperature and variations that may be observed during sample collection time shall be noted. Observations about the water (color, turbidity, etc) the filter (upon removal), or procedural activities including the presence of air in the sampling lines during water collection are important notes to be recorded. All field analyses shall be documented.
- 9) At the conclusion of a day's sampling activities, repeat the performance tests as described in section 5.1 and record the results.

5.3 Acidification

Some samples (see Table 1) require acidification. Acidification should be performed within 12 hours of sample collection.

Equipment: Ultra-pure (double-distilled or triple-distilled) HNO_3 . Alternately, an acid blank shall be supplied as a sample along with any acidified samples.

Summary of method: Add acid to filtered sample to obtain a pH of 2 or less.

5.4 Cations/Metals:

5.4.1 Cations: Si, Na, Ca, K, Mg, B, S, Fe, Li, Sr

Equipment:

- 1) Filtration equipment listed in Section 5.2
- 2) Acidification materials listed in Section 5.3
- 3) 20 ml or larger polyethylene container.

Method:

- 1) Filtration shall employ a filter pore size of 0.45 μm or less. Record filter pore size used.

- 2) Fill the bottle with filtrate. Samples shall be acidified to a pH of about 2 or less (about 2 ml HNO₃ per liter).
- 3) Cap and seal.

5.4.2 Cations: Al

Equipment:

- 1) Filtration equipment listed in Section. 5.2.
- 2) 20 ml or larger polyethylene container.

Method:

- 1) Filtration shall employ a filter size of 0.10 µm or less. Record the filter pore size used.
- 2) Fill the bottle with filtrate.
- 3) Cap and seal.

5.5 Anions

Equipment:

- 1) 10 ml or larger polyethylene bottles.
- 2) Filtration equipment listed in section 5.2

Method:

- 1) Filtration shall employ a filter pore size of 0.45 µm or less (0.1 µm is preferable, but not required). Record the filter pore size used.
- 2) Rinse the cap and bottle several times with filtrate (if sufficient quantity).
- 3) Fill the bottle with filtrate, selecting the bottle size to ensure that sufficient quantity is available to completely fill and therefore minimize head space.
- 4) Cap and seal.

5.6 Hydrogen and Oxygen

Equipment:

- 1) 40 ml or larger glass sample bottle with Teflon or polyseal cap
- 2) Filtration equipment listed in Section 5.2

Method:

- 1) Fill bottle with filtrate, filling from the bottom (and overflowing several volumes if sufficient quantity). The selection of the collection bottle size shall ensure that sufficient quantity is available for complete filling and minimization of headspace.
- 2) Cap and seal the container.

5.7 Carbon (¹³C/¹²C) and radiocarbon sample

Equipment:

- 1) Laboratory-prepared sampling vessel, brought to the field: Evacuated 40 ml glass vial capped with septa from a 7 ml Vacutainer; septa lightly greased with silicon grease and cap sealed with parafilm; 50% NaOH solution injected into evacuated vessel. Vial stored to prevent contact of septa with NaOH.
- 2) ~50 cc luer-lock syringe, 0.45 μ m syringe tip filter and needle.

Method:

- 1) A tee-connector with an on/off luer-lock connecting valve is placed in the sampling line in a convenient location before flow through the pump head. After at least 500 ml of water has been sampled from the interval, a carbon isotope sample may be captured. The fluid flow in the tubing should be liquid-filled. Attach a syringe (~50 cc syringe) with luer-lock connector to the valve located in the sampling line.
- 2) To avoid bubbles forming in the syringe, draw in and flush with 10-20 ml sample several times before final sample collection. Slowly draw 20 ml of water out of the sampling line into the syringe. Remove from tee-port.
- 3) Sample may be filtered through a 0.45 μ m syringe tip filter. By attaching a needle to the syringe, the filtrate may be injected directly through the septa of the evacuated and prepared sample vial.
- 4) Collect replicate samples if sample quantity allows.

5.8 Uranium

Equipment:

- 1) 40 ml or larger polyethylene, pre-cleaned bottle.
- 2) Acidification materials listed in section 5.3.
- 3) Filtration equipment listed in section 5.2.

Method:

- 1) Filtration should ideally employ a filter pore size of 0.10 μ m or less, but 0.45 μ m is okay. Record filter pore size used.
- 2) Samples must be acidified to a pH of about 2 or less (about 2 ml HNO₃ per liter).
- 3) Cap and seal.

5.9 Strontium

Equipment:

- 1) 40 ml or larger polyethylene bottle and Teflon or polyseal cap.
- 2) Filtration equipment listed in section 5.2.

Method:

- 1) Filtration should ideally employ a filter pore size of 0.45 μ m or less. Record filter pore size used.
- 2) Fill the bottle with filtrate, selecting the bottle size to ensure that sufficient quantity is available for complete filling and minimization of head space.
- 3) Cap and seal.

5.10 Total Carbon/Total Organic Carbon/Total Inorganic Carbon

Equipment:

- 1) *method a:* pre-cleaned 10 ml (or larger) glass bottle and cap

- 2) *method a*: Filtration equipment listed in section 5.2.
- 3) *method b*: 50 cc gas-tight syringe with luer-lock connection, and needle; pre-cleaned 10 ml (or larger) glass bottle and septa-lined cap; syringe tip filters
- 4) *methods a and b*: Cooler, or means to maintain temperature of ~ 4°C

Summary of Methods (use either *a* or *b*):

Method a

- 1) Filter (0.45 µm) sample directly into collection bottle if possible; use a reducer to direct flow into sample collection bottle if necessary
- 2) Fill the bottle with filtrate, selecting the bottle size to ensure that sufficient quantity is available for complete filling.
- 3) Cap immediately to minimize exposure to atmosphere. Avoid agitation.
- 4) Store at ~4°C and keep from light. Sample shall be analyzed within 24 hrs or as soon as possible after collection.
- 5) Collect replicate sample if sufficient quantity.

Method b

- 1) Alternately, acquire sample from the tee-port configured for the carbon isotope samples using a ~50 cc gas-tight syringe with luer-lock connection. (See section 5.7) First flush the syringe with 10-20 ml samples of water several times and then collect 40-50 ml. Remove the syringe from tee-port.
- 2) Attach a syringe-tip filter and needle and carefully, so as to prevent bubble formation, inject the sample through septa in cap. Fill the vessel completely. Avoid agitation.
- 3) Store at ~4°C and keep from light. Sample shall be analyzed within 24 hrs or as soon as possible after collection.
- 4) Collect replicate sample if sufficient quantity.

TABLE 1. SUMMARY OF SAMPLES FOR DESIGNATED CHEMICAL ANALYSES

Sample Type	Container	Volume*	Filter Pore Size	Preservation	Ship To:**
General Purpose	Polyethylene	2ml - 500ml (default: 60ml)	0.1-0.45 µm	None	LLNL
Cations/Metals	Polyethylene	2ml - 100ml (default: 30ml)	0.1-0.45 µm	~1ml HNO ₃ per liter (to pH<2)	LBNL
Anions	Polyethylene	30ml - 500ml (default: 60ml)	0.1-0.45 µm	None	LLNL
Al	Polyethylene	250ml	0.1 µm	None	LLNL
²³⁴ U/ ²³⁸ U	Polyethylene	50 ml- 500ml(default: 500ml)	0.1-0.45 µm	None	USGS
⁸⁷ Sr/ ⁸⁶ Sr	Polyethylene	50 ml- 500ml((default: 500ml)	0.1-0.45 µm	None	USGS
¹⁴ C	See method	40ml	N/A	See method	LBNL
¹³ C/ ¹² C	See method	40ml	N/A	See method	LBNL
Total Carbon, TIC/TOC	Amber glass or clear glass	125ml	0.1-0.45 µm	Chill/dark	LLNL
¹⁸ O/ ¹⁶ O and ² H/H	Glass, no rinse, dry bottle	60-125ml	0.1-0.45 µm	None	LBNL

*Low value is minimum sample needed for analysis. High value assumes unlimited sample volume.
Default value is typical volume selected when total volume is sizable but not unlimited.

**Destination of sample may change at discretion of the PI.

5.11 Alkalinity/HCO₃/CO₂ (method for using Hach Co. field analysis kit)

This analysis is QA:NA, and is rarely feasible due to the large quantities of sample required. If there is not enough sample to perform this analysis, a QA:NA estimate of total alkalinity can be obtained using colormetric test strips.

Equipment:

- 1) Digital titrator
- 2) Alkalinity reagent set which includes Bromcresol Green-Methyl Red powder pillows, Phenolphthalein powder pillows, DI water; sulfuric acid titration cartridge 1.600 N and 0.1600N
- 3) Erlenmeyer flask, 250 ml
- 4) Graduated cylinders in various sizes (10, 25, 50 and 100 ml)

Method:

The sample is titrated with sulfuric acid to a colorimetric end point corresponding to a specific pH. Phenolphthalein alkalinity is determined by titrating to a pH of 8.3, as evidenced by the color change of phenolphthalein indicator, and indicates the total hydroxide and one half the carbonate present. M (methyl orange) or T (total) alkalinity is determined by titration to a pH between 3.7 and 5.1, and includes all carbonate, bicarbonate and hydroxide.

- 1) Samples shall be analyzed as soon as possible after collection. Select the sample volume and the sulfuric acid (H₂SO₄) Titration Cartridge corresponding to the expected alkalinity concentration as mg/L calcium carbonate (CaCO₃):
- 2) For an anticipated range of 10-40 mg/L as CaCO₃ a sample volume of 100 ml is required with the 0.1600 N H₂SO₄ cartridge
- 3) For an anticipated range of 40-160 mg/L as CaCO₃ a sample volume of 25 ml is required with the 0.1600 N H₂SO₄ cartridge
- 4) Or for an anticipated range of 100-400 mg/L as CaCO₃ a sample volume of 100 ml is required with the 1.600 N H₂SO₄ cartridge
- 5) Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body.
- 6) Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip with a clean lint-free wipe.
- 7) Use a graduated cylinder or pipet to measure the sample volume. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about 100-mL mark with DI water, if necessary.
- 8) Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix.
- 9) If the solution turns pink, titrate to a colorless end point. Place the delivery tube tip into the solution and swirl the flask while titrating with sulfuric acid. Record the number of digits required. (If the solution is colorless before titrating with sulfuric acid, the *P* alkalinity is zero; proceed to step 11.)
- 10) Calculate: required titrator digits x *digit multiplier* = mg/L CaCO₃ *P* alkalinity where the *digit multiplier* used is:
 - 0.1 if step 2) above is followed: 10-40 mg/L CaCO₃
 - 0.4 if step 3) above is followed: 40-160 mg/L CaCO₃
 - 1.0 if step 4) above is followed: 100-400 mg/L CaCO₃
- 11) Add the contents of one Bromcresol Green- Methyl Red Indicator powder pillow to the flask and swirl to mix

- 12) Continue the titration with sulfuric acid to a light greenish blue-gray (pH 5.1), a light violet-gray (pH 4.8), or a light pink (pH 4.5) color, as required by the sample composition:
- Sample composition alkalinity ~30 mg/L requires end-point pH 5.1
 - Sample composition alkalinity ~150 mg/L requires end-point pH 4.8
 - Sample composition alkalinity ~500 mg/L requires pH 4.5
 - if silicates or phosphates present pH 4.5 Record the number of digits required.
- 13) Calculate: total digits x digit multiplier = mg/L CaCO₃ Total (*T or M*) alkalinity
NOTE: Carbonate, bicarbonate and hydroxide concentrations may be expressed individually using the relations shown in Table 2.

TABLE 2: FIELD ANALYSIS OF ALKALINITY

Results of Titration	Hydroxide Alkalinity is equal to:	Carbonate Alkalinity is equal to:	Bicarbonate Alkalinity is equal to:
Phenolphthalein Alkalinity = 0	0	0	Total Alkalinity
Phenolphthalein Alkalinity = Total Alkalinity	Total Alkalinity	0	0
Phenolphthalein Alkalinity is less than one half of Total Alkalinity	0	2 times the Phenolphthalein Alkalinity	Total Alkalinity minus 2 times the Phenolphthalein Alkalinity
Phenolphthalein Alkalinity is equal to one half of Total Alkalinity	0	2 times the Phenolphthalein Alkalinity	0
Phenolphthalein Alkalinity is greater than one half of Total Alkalinity	2 times the Phenolphthalein Alkalinity minus Total Alkalinity	2 times the difference between total and Phenolphthalein Alkalinity	0

6.0 QA RECORDS

QA records, and any corrections or changes generated as a result of implementing this procedure shall be prepared and submitted as inclusionary QA records (QA:QA) by the PI or designee in accordance with AP-17.1Q, *Records Management*. These records include:

- 1) Performance Test results (section 5.1)
- 2) Sample volumes and sampling start and stop times (section 5.2)
- 3) Field analyses results (section 5.2)

7.0 REFERENCES

7.1 Implementing Documents

QAIP 20-1, Technical Procedures

AP16.1Q, Condition Reporting and Resolution

AP-17.1Q, Records Management

7.2 Applicable Standards, Criteria, and Manufacturer's Guidance

Ultrameter Operation Manual – Model 6P, Myron L Company, Carlsbad, CA